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1-(3, 4-dichlorobenzenesulfonyl)-3-methyl-1*H*-imidazolium chloride: An efficient catalyst for the synthesis of 1, 8-dioxo-octahydroxanthenes under microwave irradiation

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Abstract

The reaction of 5,5-dimethyl-1,3-cyclohexanedione with various aromatic aldehydes to give corresponding 1,8-dioxo-octahydroxanthenes in aqueous medium has been reported. These reactions were carried out under microwave irradiation and catalyzed by 1-(3, 4-dichlorobenzenesulfonyl)-3-methyl-1H-imidazolium chloride. A plausible mechanism for the synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by[3, 4-dcbsmim][Cl] in water has been given.

Keywords: Aldehydes, 1-(3, 4-dichlorobenzenesulfonyl)-3-methyl-1H-imidazolium chloride ([3,4-dcbsmim][Cl]), 5,5-dimethyl-1,3-cyclohexanedione, 1,8-dioxo-octahydroxanthenes, Microwaves, Water.

1. INTRODUCTION

Xanthenes constitute an important class of biologically active compounds because of its wide range of biological and pharmaceutical properties such as anti-inflammatory, antidepressants and antimalarial agents [1]. They act as sensitizers in photodynamic therapy (PDT) for destroying the tumor cells[2]. Xanthenes are also used in the dye industry[3], in cosmetics and pigments[4], in laser technology because of their spectroscopic properties[5], etc. Xanthenes based dyes are extracted naturally from soil and plants such as Indigofera longeracemosa[6]. They are used as pH sensitive fluorescent materials for the visualization of biomolecular assemblies[7] and also as antagonists for the paralyzing action of zoxazolamine[8].

Due to their biological and pharmacological importance, several methods have been reported for the synthesis of Xanthenes employing Lewis acids as catalysts to accelerate the condensation reaction of aldehydes with 5,5-dimethyl-1,3-cyclohexanedione in the presence of [1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate)[9], montmorillonite K10[10], $ZrOCl_2 \cdot 8H_2O$[11], heteropolyacid supported MCM-41[12], nanosized MCM-41-SO_3H[13], nano CuI[14], nanoSO_4^{2-}/xFe–Zr–O[15], silica bonded N-propyl sulfamic acid[16], Zn[L-proline]$_2$[17], [Bmim][HSO_4][18], [Hmim]TFA[19], [TMPSA]HSO_4[20], [DDPA][HSO_4][21], [Et_3N-SO_3H]Cl[22], [Hbim]BF_4[23], [Et_3NH]H_2PO_4[24], [Et_3NH][HSO_4][25],TMGT[26], p-dodecylbenzenesulphonic acid[27], trichloroisocyanuric acid[28], silica sulfuric acid[29],alumina-sulfuric acid[30],trimethylsilyl chloride[31], $NaHSO_4$-SiO_2[32], ZnO-acetyl chloride[33], CAN[34], Amberlyst-15[35], Dowex-50W[36], PMA-SiO_2[37], PPA-SiO_2[38], as catalysts and also in ionic liquid [bmim]BF_4 as solvent catalysed by $FeCl_3 \cdot 6H_2O$[39], $InCl_3 \cdot 4H_2O$[40], and $NaHSO_4$[41], $Mg(BF4)_2$ doped in [BMIm][BF_4][42] and LiBr[43], $SmCl_3$[44] etc. All the methods have their own advantages with some disadvantages such as low yields, requirement of organic solvents, use of expensive catalysts, tedious workup procedure, etc.

In recent years, ionic liquids are of considerable interest as they can serve as catalysts, green reaction media in organic synthesis and also due to their properties such as non-volatility, non-flammability, ionic conductivity[45-48]. Recently a variety of ionic liquids have been demonstrated as practical alternative to organic solvents as well as catalysts in organic reactions/transformations[49]. Recently, 1-(Benzenesulfonyl)-3-methyl-1*H*-imidazolium chlorides catalyzed electrophilic substitution reactions of indoles with various carbonyl compounds for an efficient one pot synthesis of

bis(indolyl)methanes have also been reported by our group[50]. Also the use of microwave irradiation for carrying out organic reactions has been well established in recent years[51-52] as it is an environmentally friendly method for the organic synthesis. herein, we report the catalytic application of 1-(3, 4-dichlorobenzenesulfonyl)-3-methyl-1*H*-imidazolium chlorides for the synthesis of 1,8-dioxo-octahydroxanthenes by the condensation of aromatic aldehydes with 5,5-dimethyl-1,3-cyclohexanedione using easily available, reusable ionic liquid as catalyst under microwave irradiation in aqueous media.

2. EXPERIMENTAL

All solvents and reagents were commercial and used without further purification. Melting points were uncorrected. Nuclear magnetic resonance spectra were obtained on a Bruker AMX spectrophotometer in $CDCl_3$ at 300 MHz. Chemical shifts were obtained in parts per million (δ) and were measured using tetramethyl silane (TMS) as reference. IR spectra were recorded on a Shimadzu FT-IR-8400S spectrophotometer using KBr pellets and were reported as wave numbers (ν cm^{-1}). The synthesis was carried out using modified household microwave oven (Frigidaire).

2.1. Preparation of [3,4-dcbsmim][Cl]

1-Methyl-1H-imidazole (2.0 mmol) was taken in a dry round bottomed flask at 0°C. To this 3,4-dichlorobenzenesulfonyl chloride (2.0 mmol) was added slowely and the reaction mixture stirred for 3-4 min to obtain a light yellow precipitate. The product was washed with petroleum ether, dried and stored in cool place. The compound was obtained in 95-96 % yield. [50]

2.2. General procedure for the microwave synthesis of 1,8-dioxo-octahydroxanthenes:

A mixture of aldehyde (5.0 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (10 mmol), 1-(3, 4-dichlorobenzenesulfonyl)-3-methyl-1H-imidazolium chloride ([3,4-dcbsmim][Cl]) (0.5 mmol) and 5 mL of water was taken in a closed teflon vessel. The mixture was irradiated with microwaves for a given time (Table 2). The reaction was monitored by TLC. After completion of the reaction, the product was filtered out from the water media and then re- crystallized from ethanol. Further, the filtrate (water) was vacuum evaporated to dryness to recover the catalyst [3,4-dcbsmim][Cl] and the resulting catalyst was reused directly for the next run. The products were characterized by melting points, IR, NMR & Mass spectra and compared with those reported for the authentic samples.

2.3. Spectral Data for the few compounds

2.3.1. 9-phenyl-3,3,6,6-tetramethyl-1,2,3,4,6,7,8-octahydroxanthene-1,8-dione (3a)

White solid; m.p=205-207°C. IR (KBr)(ν_{max} /cm^{-1}): 2972,1670,1360,1196. ^{1}HNMR($CDCl_3$,300MHz):δ=0.97(s,6H),1.08(s,6H),2.15-2.26(q, 4H), 2.48(s,4H), 4.72(s, 1H),7.07-7.14(m,1H),7.16-7.26(m,2H),7.36(m,2H). ^{13}CNMR ($CDCl_3$100MHz): δ=27.2, 29.2, 31.9, 32.0, 41.3, 50.3, 114.6, 126.3, 128.0, 128.3, 144.0, 163.2, 195.0. MS (EI) *m/z*350 (M^+).

2.3.2. 9-(4-chlorophenyl-3,3,6,6-tetramethyl-1,2,3,4,6,7,8-octahydroxanthene-1,8-dione (3b)

White solid; m.p=229-232°C. IR (KBr)(ν_{max} /cm^{-1}): 2960,1660,1350,1190. ^{1}HNMR($CDCl_3$,300MHz):δ=0.99(s,6H),1.08(s,6H),2.14-2.26(q, 4H), 2.46(s,4H), 4.70(s, 1H),7.16-7.42(m,4H). ^{13}CNMR ($CDCl_3$100MHz):δ=27.2, 28.1, 30.8, 31.9, 32.1, 40.7, 50.6, 115.1, 128.1, 129.0, 129.6, 142.6, 162.4, 196.3. MS (EI) *m/z*385 (M+1).

2.3.3. 9-(4-hydroxyphenyl-3,3,6,6-tetramethyl-1,2,3,4,6,7,8-octahydroxanthene-1,8-dione (3f)

White solid; m.p=245-248°C. IR (KBr)(ν_{max} /cm^{-1}): 3330,2954,1650,1360,1191. ^{1}HNMR($CDCl_3$,300MHz):δ=0.99(s,6H),1.09(s,6H),2.14-2.20(q, 4H), 2.47(s,4H), 4.63(s, 1H),5.72(s,1H), 7.16-7.02(m,4H). ^{13}CNMR ($CDCl_3$100MHz): δ=27.2, 29.1, 30.2, 31.4, 32.1, 40.6, 50.6, 115.1, 128.0, 129.0, 139.4, 140.6, 162.4, 195.3. MS (EI) *m/z*366 (M^+).

3. RESULTS AND DISCUSSION

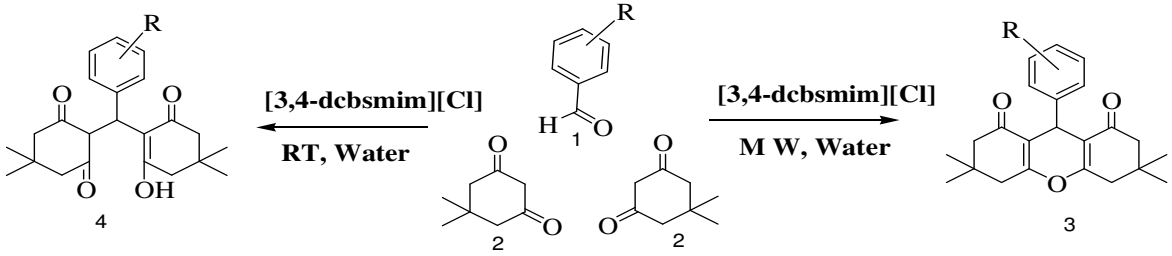
Initially, the catalyst [3,4-dcbsmim][Cl] was prepared as previously explained. In order to optimize the green reaction conditions, we firstly investigated the greener solvents on the reaction rate as well as yields of the products (Table 1). In a typical experimental procedure, the reaction of 5,5-dimethyl-1,3-cyclohexanedione (1.0 mmol) and benzaldehyde (0.5 mmol) catalyzed by [3,4-dcbsmim][Cl] (0.5 mmol) in different solvent media was investigated under microwaves. Water is found as an ideal solvent because it is inexpensive, non-flammable, abundant and environmentally benign.

To determine the optimum concentration of catalyst, we have investigated the model reaction of benzaldehyde (10.0 mmol) with 5, 5-dimethyl-1, 3-cyclohexanedione (20.0 mmol) carried out at 1, 5, 10, and 20 mol% of [3,4-dcbsmim][Cl] in water under microwave irradiation. The products were obtained in about 90, 92, 94 and 94 % yield, respectively in 3min. This indicates that 10 mol% of [3,4-dcbsmim][Cl] is sufficient for the best yield. Subsequently, all the

Table - 1: Effect of solvent in the preparation of 3,3,6,6-tetramethyl-9-phenyl-3,4,6,7-tetrahydro-2H-xanthene-1,8(5H,9H)-dione catalyzed by [3,4-dcbsmim][Cl].[a]

Entry	Solvent	Catalyst (mol %)	Time (min)	Yield (%)[b]
1	Acetonitrile(3mL) + [Bmim][Cl] (7 mL)	10	4	93
2	Acetonitrile (10 mL)	10	4	94
3	[Bmim][Cl] (10 mL)	10	4	93
4	Water (10 mL)	10	3	94
5	Neat	10	4	90

[a] Reaction conditions: benzaldehyde (0.5 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1.0 mmol), Microwaves in different solvents; [b] Isolated yield.

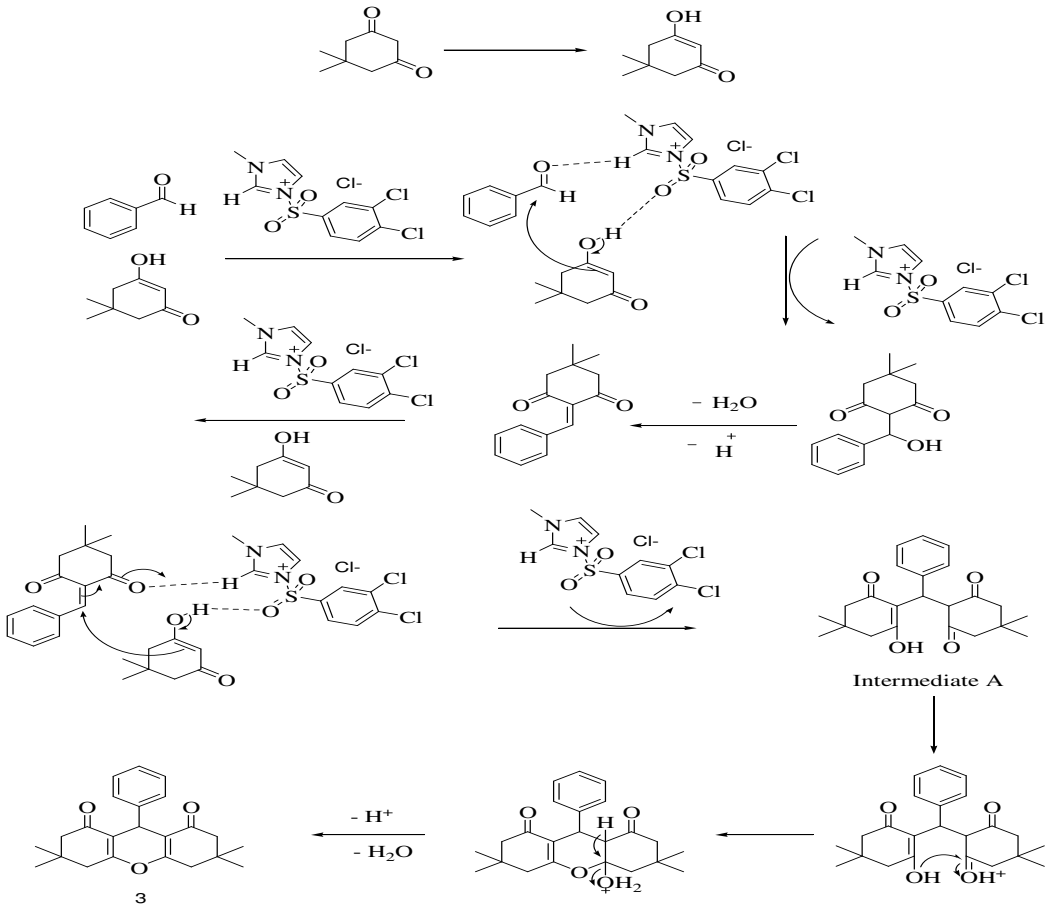


Scheme - 1: Synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by [3,4-dcbsmim][Cl].

Table - 2: [3,4-dcbsmim][Cl] catalyzed microwave synthesis of 1,8-dioxo-octahydroxanthenes.[a]

Entry	Aldehyde	Product 3	Time (min)	Yield[b] (%)	Melting point (°C)
1	Benzaldehyde	3a	3	94	205-207
2	4-Chlorobenzaldehyde	3b	4	95	229-232
3	2-Chlorobenzaldehyde	3c	5	94	225-227
4	4-Bromobenzaldehyde	3d	5	90	240-242
5	4-Fluorobenzaldehyde	3e	5	91	226-228
6	4-Hydroxybenzaldehyde	3f	5	92	245-248
7	2-Hydroxybenzaldehyde	3g	4	89	202-206
8	4-Methoxybenzaldehyde	3h	5	90	240-242
9	3-Methoxybenzaldehyde	3i	5	95	178-180
10	4-Nitrobenzaldehyde	3j	3	92	224-226
11	3- Nitrobenzaldehyde	3k	5	93	170-172
12	4-Tolualdehyde	3l	4	90	208-209
13	2,4-Dichlorobenzaldehyde	3m	5	91	247-249
14	Cinnamaldehyde	3n	4	90	178-180
15	4-Hydroxy-3-methoxybenzaldehyde	3o	5	85	226-228

[a] Reaction conditions: aromatic aldehyde (0.5 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1.0 mmol), [3,4-dcbsmim][Cl] (0.5 mmol) , Microwave irradiation, in aqueous medium; [b] Isolated yield.



Scheme - 2: Plausible mechanism for the synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by[3, 4-dcbsmim][Cl] in water.

Table - 3: Recycling of the catalyst.[a]

Run	Time(min)	Yield [b] (%)
1	3	92
2	3	90
3	4	87
4	4	85

[a] Reaction conditions: 4-nitro benzaldehyde (0.5 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1.0 mmol), [3,4-dcbsmim][Cl] (0.5 mmol) , Microwaves, in aqueous medium; [b] Isolated yield.

reactions (Table 2) were carried out under microwave in presence of 10 mol% of [3, 4-dcbsmim] [Cl] in aqueous conditions for the preparation of 1,8-dioxooctahydroxanthenes (3) (Scheme 1) and the expected product was obtained in good yield. Also at room temperature we obtained the first dehydration product of dimedone and aromatic aldehyde, that is, 2,2′-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexane-1-one (Intermediate A), as shown in scheme 2. The second dehydration step requires heating to remove water to afford the target 1,8-dioxooctahydroxanthenes (3).

In order to demonstrate the reusability of [3,4-dcbsmim][Cl] the experiment was performed using 4-nitrobenzaldehyde as a model substrate under aqueous condition. The product was recrystallized from 95% ethanol to obtain the desired product in pure form. The water layer consisted of [3,4-dcbsmim][Cl] along with some residual reactants and byproducts, and vacuumed to get catalyst with impurities. The resulting catalyst was directly used in subsequent runs without further treatment (Table 3).

The ionic liquid [3,4-dcbsmim][Cl] can be recycled for at least 3-4 times without any loss in catalytic activity. The efficacy of [3,4-dcbsmim][Cl] in the synthesis of Xanthenes in comparison with the other ionic liquids as reported in the literature can be understood from the results shown in table 4.

Table - 4: Comparison of ionic liquids used as catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes.[a]

Entry	Ionic liquid	Conditions	Time (min)	Yield (%)[b]	Reference
1	[Bmim] HSO_4	100 °C	25	93	18
2	TMGT/TFA	75 °C	20-30	92	26
3	$[Et_3NH][H_2PO_4]$	100 °C	5	96	24
4	$Mg(BF_4)_2$ doped in [Bmim][BF_4]	80 °C	30	97	42
5	$[Et_3NH][HSO_4]$	100 °C	20	94	25
6	No Catalyst	Water, MW	7	80	-
7	[3,4-dcbsmim][Cl]	Water, MW	3	94	Present work

[a] Reaction conditions: benzaldehyde (0.5 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1.0 mmol) at different conditions; [b] Isolated yield.

4. CONCLUSION

In conclusion,1-(3,4-dichlorobenzenesulfonyl)-3-methyl-1*H*-imidazolium chloride [3,4-dcbsmim][Cl] has proven to be an efficient and recyclable catalyst for the synthesis of xanthene derivatives under microwave irradiation.. The method is simple, clean, and green. The recycled ionic liquid can be reused for 3-4 cycles without loss in catalytic activity.

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